A STUDY OF THE MIGRATION OF IONS IN GLASS

BY

JOSEPH ADAM PASK

B.S., University of Illinois, 1934

M.S., University of Washington, 1935

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
ENGINEERING IN THE GRADUATE SCHOOL OF
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A STUDY OF THE MIGRATION OF IONS IN GLASS

I. INTRODUCTION

The study of migration of ions in glass is directly associated with that of diffusion since migration of any type will not occur unless forces promoting diffusion are present. Considerations are presented regarding the practical importance of the problem of diffusion in chemical-physical processes and in ceramic problems.

This research was made to study the nature of and the rates of diffusion from a number of salts, primarily silver, into a commercial flint glass, i.e. soda-lime-silica glass.

II. LITERATURE

Literature on the subject of diffusion, especially in glasses, is relatively meager. Fick's law has been the fundamental basis for the study of diffusion in liquids on a quantitative basis. This law states that the driving force which impells a dissolved substance to move from the place in the solution of higher concentration to one of lower concentration, and which also determines the rapidity of the movement of the particle is proportional to the drop in concentration. Assuming that the diffusion coefficient is a constant, which is true for specifis cases, the following diffusion equation is obtained:

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

If one solves for D in this equation and combines the constants, then a relationship is derived that the amount of material migrating in per square centimeter is directly proportional to the square root of time. This has been found to hold by previous workers on the subject of diffusion of silver into glass in their experimental range. Schulze, Halberstadt, and Kubaschewski worked in the temperature range up to the softening point of the glass and in one case up to the point of appreciable lowering of viscosity. Several theories as to the nature of the diffusing particles had been reported.

Other references on diffusion in silicate melts are those of Endell and Bowen. The Ludwig-Soret phenomena was demonstrated by Wessels. Endell also makes reference to Liesegang rings in agates and their theory of formation.

III. EXPERIMENTAL PROCEDURE

The samples were prepared in the form of cups with thick walls. They then acted as the containers for the diffusing material. Thus, with the use of a special Alundum crucible these sample cups were able to be used for tests up to 1100°C. Tests were maintained at constant temperature for as long as 108 hours. The diffusing materials were salts of the elements listed under Results.

The cups were cut in half vertically and the distance of duffusion was measured. The colors were noted and a spectrophotometer used to obtain a transmittance curve for various wavelengths for one of the samples. An indication of silver concentration and the nature and size of particles was obtained with use of the spectrograph, ultramicroscope, and X-rays.

IV. RESULTS

The most complete results were obtained with silver nitrate as a source of diffusing particles. Plotting time against distance of diffusion at 500 and 900°C it is found that the rate of diffusion is not constant but falls off with time. Also, curves showing relation of temperature to distance of diffusion are presented for test times of 12 and 108 hours. The distance of penetration is accelerated in the region of the softening temperature of the glass, and likewise an acceleration would probably also occur in the temperature region of rapid decrease of viscosity.

A marked change in the nature of diffusion at the softening temperature of the glass is also indicated by a sharp change of slope in drawing the curve for silver concentration against distance of diffusion.

If Fick's law holds with a constant diffusion coefficient, then grams per square centimeter are proportional to the

square root of time. With the plotting of these values a straight line was obtained at first but it deviated after about 36 hours test time.

In a sample heated at 900°C. for 36 hours it was found that the percent concentration gradient fell continuously from the interface surface even though the concentration of the number of particles did not. The colors of the samples after diffusion were shades of yellow, amber, and brown due to different sized particles and aggregations.

Other silver salts also tried were the chloride, the oxide and the sulphate. The curves obtained were, in general, similar to those above. Diffusion from the chloride was found to be approximately twice as fast. A reducing atmosphere reduced the diffusion rate from the oxide but not from the chloride.

A Liesegang ring effect was observed in some of the specimens with silver salts as a source of diffusion at temperatures above the softening point of glass.

Testing a number of non-silver salts, Au, Co, Cu, Cr, Fe, Pb, Pt, Tl, V, it was found that copper, thallium and vanadium were the only ones that showed diffusion. Their rates, however, were not as fast as that for silver. Copper colored the glass blue and the others were colorless.

V. DISCUSSION

The occurrence and rate of diffusion is dependent on both the glass and the salt providing the diffusing particles.

Two types of diffusion are present:—replacement of alkali ions within the glass or penetration of particles of some kind into the holes of the glass. The former type is present at all times providing ions from the salt are available and, in general, it is the predominant type for cases at temperatures below the softening point of the glass. The latter type is commonly present, usually in addition to the former, at temperatures above the softening point. Here, the expansion of the glass and the breaking of bonds in the glass structure form openings for passage of larger particles.

The source of diffusing particles is a primary controlling factor in the process. Diffusing particles, simple or complex ions, atoms or molecules, must be formed and they must be of proper size to penetrate into the glass openings. These particles can be provided in one of the following ways: a) molten salt with sufficiently high ionization constant at the test temperature, b) sufficiently high vapor or dissociation pressure, and c) reaction with the glass.

Below the softening point the glass offers greater resistance to entrance of ions than to movement of ions and consequently the volume concentration drops rapidly with distance of penetration. Above the softening point the entrance of particles is as fast as the movement of them through the glass and thus there is no appreciable drop in concentration with distance of penetration. This reduced resistance also facilitates the formation of aggregates whose size is dependent upon the concentration of silver in the region. Variation in concentration thus causes bands of different colors. The state of aggregation in one of these bands is apparently more sensitive to thermal changes resulting in a number of narrower bands which resemble Liesegang rings.

Movement of complex ions into glass is indicated to some extent by reactions in the glass surface accompanied by the evolution of a gas and by the effect of the atmosphere on rate of diffusion in cases where the salts contain oxygen.

VI. SUMMARY

Of the salts tested, those of silver, thallium, and vanadium diffused. The increasing order of ionic sizes is vanadium, silver, and thallium, which also approximately corresponded to the rates of diffusion. Copper salts showed a reaction with the glass with a possible diffusion. If that were the case, the diffusing particle probably was a complex one since its apparent diffusion was much less than that for silver though its cation is smaller than the silver cation.

The rate of diffusion for silver nitrate at a given temperature is practically constant up to about 10 hours test time

and then falls off. In 36 hours, the distance of diffusion at 900° C. is 0.43 cm. and at 500° C is 0.05 cm. Silver chloride at 900° C. is 0.8 cm.

The increase of diffusion for a given time with temperature rise is more rapid. A break is shown at the softening temperature and another is probably present at the temperature of rapid decrease of viscosity.

Concentration of silver from silver nitrate with distance of diffusion shows a sharp change at the softening temperature of the glass.

Fick's law, as generally given, holds for a limited time at the beginning of the experiment. Consequently, the so-called diffusion constant is not constant throughout the entire test period.

The concentration gradient is a straight line approaching the distance axis asymptotically. Therefore, the size of the particles in the colored bands in the specimens above the softening point do not vary progressively since the number does not vary progressively.

In the gray diffusion portions, with silver, Liesegang rings were found to occur under certain experimental conditions.

VITA

Joseph Adam Pask was born in Chicago, Illinois, February 14, 1913. He attended Lindblom High School in that city. On graduation he entered the University of Illinois where the degree of Bachelor of Science in Ceramic Engineering cum Laude was obtained in June, 1934. He then received a Cooperative Fellowship offered by the U. S. Bureau of Mines and College of Mines at the University of Washington in Seattle, Washington, where he obtained the degree of Master of Science in Ceramic Engineering in June, 1935. This was followed by a position as Ceramic Engineer at the Williamina Clay Products Co. in Willamina, Oregon. After a year he returned to the University of Illinois on an Engineering Experiment Station Fellowship. In February, 1938, he joined the teaching staff as Assistant, followed by an Instructorship in September, 1938. During the summer of 1941 he worked as Assistant Ceramic Engineer at the Electrotechnical laboratory of the U. S. Bureau of Mines in Norris, Tennessee. In September, 1941, he is joining the staff at the University of Washington as Acting Assistant Professor and head of the Department of Ceramic Engineering.

Publications are as follows:

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